# Supporting Online Material for

## Carbenes as Catalysts for Transformations of Organometallic Iron Complexes

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# Supporting Online Material

**General Considerations:** All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Solvents were deoxygenated and dried by thorough sparging with Ar gas followed by passage through an activated alumina column. Reagents were purchased from commercial vendors and used without further purification. $Fe(COT)_2$(S*1*) and the NHCs(S*2*) were prepared according to literature procedures. Elemental analysis was carried out at Desert Analytics, Tucson, AZ. NMR spectra were recorded at ambient temperature on Varian Mercury 300 and 500 MHz spectrometers. $^1$H NMR chemical shifts were referenced to residual protio solvent. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker KAPPA APEX II diffractometer.

**Preparation of mixed-valent Fe(0)-Fe(I) species (3).**
To a screw cap vial, containing a solution of $Fe(COT)_2$ (250 mg, 0.947 mmol) in pentane (100 mL), was added NHC **2** (145 mg, 0.473 mmol). After addition of the carbene the vial was capped and shaken by hand until all of the solid dissolved. The reaction vial was subsequently allowed to rest undisturbed for 2 hours, where upon black blade shaped crystals formed. The crystals were collected and washed with pentane (4 x 10 ml) to afford **3** (235 mg, 79 %). X-ray quality crystals were grown by following the procedure outlined above, but in the presence of several drops of toluene. $^1$H NMR ($C_6D_6$): δ = 43.61 (br, s), 5.64 (br, s), 2.45 (s), 1.94 (br, s), -7.33 (br, s) ppm.

**Preparation of $Fe_3(COT)_3$ (8).**
To a screw cap vial, containing a solution of $Fe(COT)_2$ (2.00 g, 7.57 mmol) in benzene (20 mL), was added a catalytic amount (10 mol%) of NHC **7** (232 mg, 0.757 mmol). After addition of the carbene the vial was capped and shaken by hand until all of the solid dissolved. The reaction vial was subsequently allowed to rest undisturbed for 24 hours, where upon black rhomboidal crystals formed. These X-ray quality crystals were collected and washed with toluene (4 x 10 ml) to afford **3** (811 mg, 67 %). If the reaction is conducted at 45$^o$C the yield of $Fe_3(COT)_3$ increases (1.15 g, 95%). To aid in solubilizing **8** for NMR analysis, briefly (15 sec.) stir the crystals in $C_6D_6$ at 80$^o$C. $^1$H NMR ($C_6D_6$): δ = -3.15 (br, s) ppm. Anal. Calcd. for $Fe_3(COT)_3$: C, 60.06; H, 5.04; Fe, 34.90. Found: C, 58.76; H, 4.43; Fe, 33.0. Complex **8** is extremely sensitive and in powdered form spontaneously ignites when exposed to air. The discrepancy between the calculated and measured elemental distributions of **8** is attributed to small amounts of adventitious air penetrating the sample container during shipping and handling.

**References**

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S2. K. M. Kuhn, R. H. Grubbs, *Org. Lett.*, **10**, 2075 (2008).